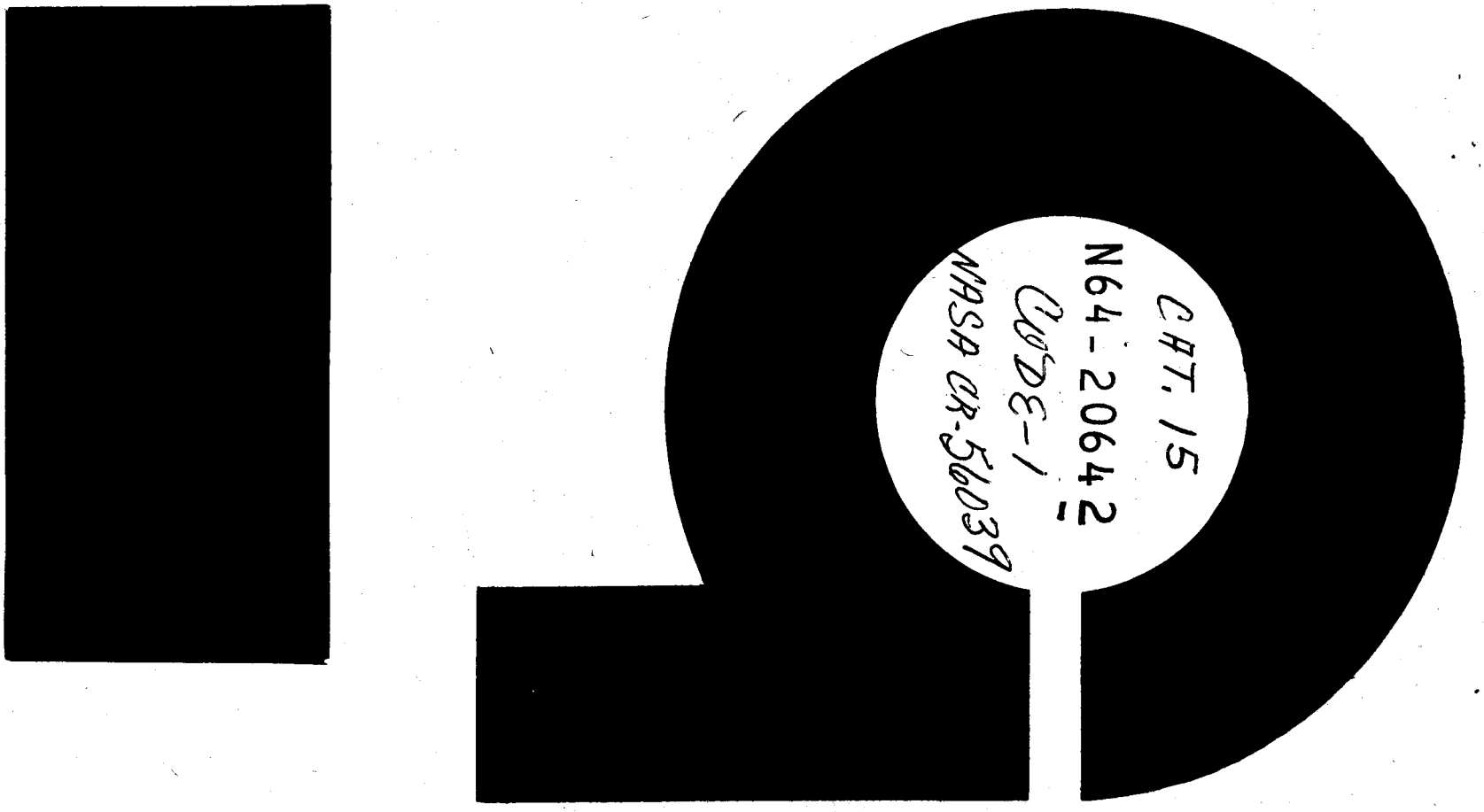

GEOPHYSICS CORPORATION OF AMERICA BEDFORD, MASSACHUSETTS

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NASA, Headquarters
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Bedford, Massachusetts

SOLIDS MASS SPECTROMETER

Second Quarterly Technical Progress Report

Contract No. NASw-839

SOLIDS MASS SPECTROMETER

20647

During the first quarter of the contract period, the ion source and the vacuum system were rebuilt with the general aim to reduce the background of the system. During the past quarter of the contract period, the operational performance of the new system was tested, the background was re-checked and further corrective measures were taken.

Author

I. OPERATIONAL PERFORMANCE

The first step was the adjustment of the primary beam. The two adjustable electrodes of the electrostatic einzel lens were adjusted in such a way that the sharpest image spot is obtained when the center electrode is on the same potential as the duoplasmatron anode. Thus, no electrical feed-through is required and the center electrode is connected internally to the duoplasmatron anode. With an acceleration voltage of 10 kv, the diameter of the spot on the target is 0.3 mm. which is the theoretical optimum, the diameter of the ion exit hole in the duoplasmatron anode being 0.25 mm and the imaging ratio being 1:1.2.

Figures 1 to 4 show several samples after prolonged bombardment with a 10 kv, 50 μA beam of argon ions. The beam struck the samples at an angle of 30 degrees against the surface. The silver sample was bombarded continuously for 2½ hours which resulted in a hole approximately 0.5 mm deep with a tapered bottom. The cadmium sample was bombarded for about 1½ hours and the resulting hole, being closer to the edge of the sample, goes right through. The tantalum and copper samples were bombarded intermittently at different spots for different periods of time, the copper sample for a total of about one hour, the tantalum sample for a total of several hours.

The samples were not cooled during these runs, but even with the low melting cadmium (321°C) no melting could have occurred, since the edges and walls of the hole had a sharp and crystaline appearance, different from that of metal solidified from the liquid state. This is also illustrated by the furrows visible on the sputtered copper surface. As was to be expected, the tantalum has a much lower total sputtering yield than the other metals.

The spot on the target can be moved from the axis in either direction by about 1 mm by means of the two pairs of mutually perpendicular deflection plates which the primary beam passes after the einzel lens. This adjustment is used to line up the spot with the axis of the secondary ion optics, which is done in practice by adjusting for highest output on the mass analyser. The target can be moved during operation perpendicular to its surface, which allows to compensate for different thickness of different samples, and in two mutually perpendicular directions parallel to its surface, which facilitates exposing different areas of the surface to the primary beam.

The 6-inch mercury diffusion pump with the liquid nitrogen cooled baffle keeps the pressure in the ion source housing around 10^{-6} torr. The base pressure of the system with closed gas inlet valve is 8×10^{-8} torr.

The beam intensity can be varied between 30 μA and 120 μA by variation of the arc supply voltage. The secondary ion intensity follows the variation of the primary beam intensity in an essentially linear manner, as can be seen on Figure 5. This is in contrast to a hypothesis that the secondary ions might be formed by ionization of sputtered neutrals by the primary beam, which would call for a square law dependence of the secondary ion intensity from the primary beam intensity. The curve is actually slightly bent the opposite way, which could be the result of beam spreading with higher intensity.

II. BACKGROUND

It had been anticipated that the replacement of the oil diffusion pumps by sputter-ion pumps could create a problem in that charged particles and ultraviolet light could escape from the Penning discharge taking place in the pumps and introduce noise in the multiplier. Care had been taken, therefore, to connect these pumps at an angle with the analyser housing so that there was no direct optical path between the pumping ports and the multiplier input. Nevertheless, it turned out that the operation of these pumps did introduce noise in the multiplier. This happened not only with the pump mounted close to the multiplier, but even with the pump mounted on the opposite end of the analyser in which case particles or photons have to collide many times with the walls of the apparatus in order to get to the multiplier. This background signal was not affected by the magnetic analyser field (up to 12,000 gauss) which is located between the sputter-ion pump and the multiplier.

Also, installation of an optical baffle in the pump connection brought no improvement. The nature of that noise is still not clear. One suggestion is that it is caused by light emitted from decaying metastables, which are formed in the discharge and diffuse about in the analyser. Whatever the cause is, the pumps are now shut off during runs and a sorption pump is being installed to keep the pressure at a sufficiently low pressure during the runs.

The major effort during this period of the contract was directed to produce a primary beam of argon ions which is essentially free of any contaminants. The importance of this task for any trace analysis comes from the fact that some

of the contaminants of the primary beam are continuously deposited on the target and sputtered togehter with the target material. Since, those contaminant elements have to be excluded from the trace analysis, it is of prime importance to have the primary beam as pure as possible.

The composition of the primary beam was investigated by the following method: After adjustment of all the controls for maximum output of the main target peak, the mass analyser is tuned to the mass 40-peak of argon. Then the primary beam accelerating voltage is reduced until the output shows a sharp maximum. This happens, when the primary beam voltage equals the target voltage, because then the field in front of the target acts as an "ion mirror" and reflects the ions. A good fraction of them are accelerated by the secondary ion optics and analysed in the mass spectrometer.

The argon passes through a liquid nitrogen cooled trap before it enters the duoplasmatron. The primary beam delivered by the oil-cooled duoplasmatron showed many background peaks (Figure 6), mainly hydrocarbons. A close inspection of the duoplasmatron after a prolonged period of operation revealed the following situation: The circular channel which carried the coolant was sealed against the arc chamber by two Viton "O" rings which were compressed between a smooth metallic and a polished ceramic surface (See Figure 1 of GCA Technical Report 63-7-G). Even though these seals are vacuum tight as tested with a helium leak detector, they did not prevent the transformer oil, used as coolant, from creeping through into the arc chamber. A radical remedy for this situation was the replacement of the oil cooled duoplasmatron by an air cooled version of otherwise very similar construction. Figure 7 shows the result of this improvement: the hydrocarbon background is greatly reduced, and above mass 65 completely eliminated.

The next suspect responsible for the remaining impurities in the primary beam was the filament. The filaments used up to then were fabricated out of platinum mesh (.004 inch wire) which was cut into ½-inch by 2-inch strips, rolled up, soaked in chemical R-500, a suspension of barium carbonate in n-butyl acetate and n-butyl alcohol, dried and then activated by heating in vacuum, which reduces the barium carbonate to oxide and is also supposed to drive out the binder. It was suspected that this type of filament continued to release hydrocarbons after activation, and also that the barium contained impurities, such as sodium and potassium which show up in the spectrum.

Subsequently, this filament was replaced by a tungsten wire containing 2% thorium. Furthermore, in order to eliminate the strong iron and copper peaks, the baffle electrode was lined with a thin-wall tantalum inset, and the anode was modified, so that all the walls in contact with or close to the arc are now out of tantalum. Figure 8 shows the result: The hydrocarbon peaks are completely eliminated. What is left are the tantalum peak in a concentration of 40 p.p.m., and the sodium and iron peaks in a concentration of 20 p.p.m. as compared with the argon peak. With a fresh filament, also the tungsten peaks appear in about the same concentration as the tantalum peak.

The only disadvantage of the tungsten filament is that it has to be operated at higher temperatures to give enough emission resulting in a shorter life (a few weeks of intermittent operation) as compared to the previously used filament which lasted for months.

Worth mentioning is that the water peak is extremely small. This indicates that the contribution of residual atmospheric gases to the background is also negligibly small. The virtual absence of a peak at mass 15 (CH_3^+), which is

a strong peak in any hydrocarbon spectrum, indicates the absence of a considerable hydrocarbon background.

The last problem still to be solved, as far as background is concerned, is the suppression of scattered ions, noticeable especially as randcm noise in the higher mass range. It is expected that the installation of diaphragms with small apertures along the beam path in the analyser will limit the beam width, eliminate most of the scattered ions, and cure this problem.

III. SPECTRA OF SOLID SAMPLES

After the primary beam was essentially free of contaminants, secondary ion spectra were taken of spectrographically pure samples and of certified standards obtained fron NBS. Figures 9 to 12 show typical spectra obtained from some of those samples. The spectra were taken after at least one-half hour of continuous bombardment, so that surface layers were certainly removed. For the silver, copper and cadmium samples, the impurities were estimated to be in the order of p.p.m. according to the spectroscopic analysis (See attached analysis reports). For the iron sample (NBS Standard #465) the certified concentrations are listed in Table 1 together with the observed relative peak heights.

Those peaks which are much stronger in the iron alloy #465 than in the supposedly pure samples can be correlated unambiguously to the actual concentrations. However, comparison with the "pure" elements shows many peaks which should either not be present there at all or at least be much smaller. The striking fact is that the intensity of these peaks varies considerably within these four samples which makes it very unlikely that they are caused by instrumental background. In the case of titanium, for example, considerable peaks are obtained from pure silver and cadmium samples, whereas a pure copper sample shows almost no titanium peaks at all. On the other hand, some of the peaks which are obtained from the pure samples, for instance, sodium, magnesium, silicon and potassium, are very weak or do not appear at all in the iron alloy.

One has to conclude, therefore, that most of the observed contaminants are really in the samples and not caused by a general instrumental background. The abnormal large contaminant peaks of the "pure" samples will require a more

detailed investigation. The results of the optical spectroscopy are subject to some doubts because the contaminants are at the very limit of detection. However, it seems unlikely that relatively large amounts of Si, Ti and Cr in the Ag sample could have escaped detection. A different and independent analysis of these samples will be necessary. Another possibility, which has to be explored in more detail, is that the sensitivity for one particular contaminant may depend on the nature of the main constituent. So far, experiments in this direction have been rather limited since only a few samples of known composition have been available. It will be necessary to produce samples with known amounts of artifically introduced impurities. The "memory effect", well known for mass spectroscopic gas analysis, does not have great importance for solid samples. Although, the copper sample has been analysed before the silver sample the copper peak is of medium size only and is at least partially caused by 1 p.p.m. contamination of the silver sample. However, a quantitative investigation of the memory effect will be necessary.

The determination of the detection limit for different impurities is seriously hampered by the fact that no really pure samples are available. The instrumental background cannot be observed directly; it has to be extrapolated from many samples with different amounts of impurities, accurately known by other means. A rough estimate of the achieved sensitivity can be obtained by neglecting any specific instrumental background and assuming that the limitation for the detection of any small peaks is the random noise of the instrument.

Below the mass number of the main peak the random noise is of the order of p.p.m. of the main peak. A contaminant which has a peak height of 10 p.p.m. can be easily detected in this region. The corresponding atomic concentrations

are listed in the last column in Table 1. One sees that the average detection limit is in the p.p.m. range. If on the other side the impurities found in the "pure" samples are real and the claimed detection limit of less than 1 p.p.m. for the optical spectroscopic method is correct, then the detection limit of the sputter source should be considerably lower. However, many more tests will be required before such a general statement can be made.

Table 1. Relative peak heights of impurity peaks from different samples given in p.p.m. of the main peak.

	Ag	Cu	Cd	Fe #465	Actual Concentrations in Fe #465 p.p.m.	Minimum Measurable Concentrations in p.p.m.
H^+	50	>600	1350	3200		
B^+	70	-	-	10	5	5
C^+	340	7	500	500	1720	3
N^+	190	-	-	200	(200)	10
O^+	160	120	350	2800	(105)	.6
Na^+	1200	120	200	100		
Mg^+	410	40	50	-		
Al^+	820	40	350	120,000	4100	.3
Si^+	2000	370	200	*		
P^+	20	* *	-	80	144	18
S^+	20	*	-	100	(180)	18
Cl^+	160	50	300	200		
K^+	200	40	*	-		
Ti^+	1500	< 10	250	160,000	2330	.15
V^+	180	< 10	-	700	22	.3
Cr^+	500	110	300	200	43	2
Mn^+	-	70	*	1800	325	2
Fe^+	1200	100	*	1,000,000	1,000,000	
Ni^+	-	-	*	400	250	6
Cu^+	180	1,000,000	400	200	167	8
Ba^+	180	-	-			
Ta^+	70	70	450			

* interference with multiple charged ions of the main constituent.

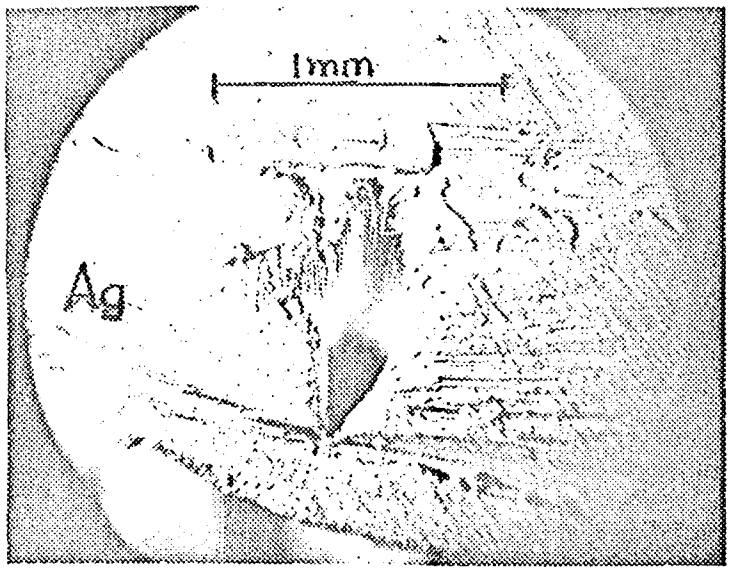


Figure 1. Silver

Figure 2. Cadmium

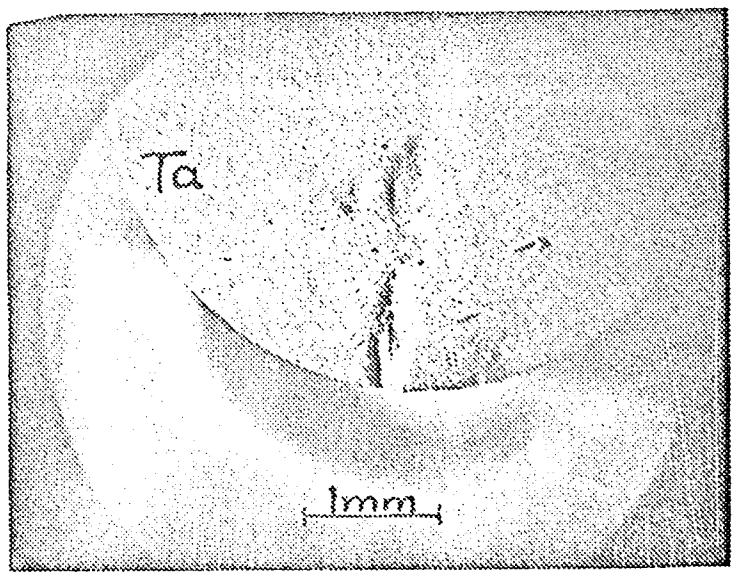


Figure 3. Tantalum

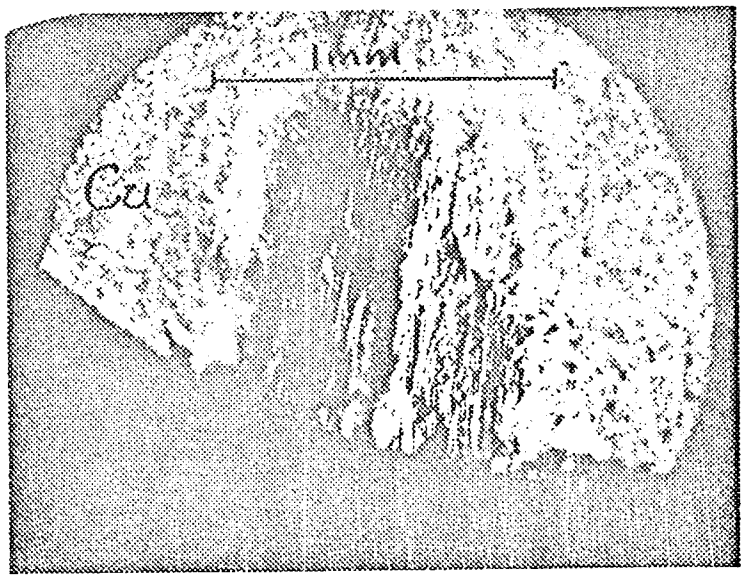
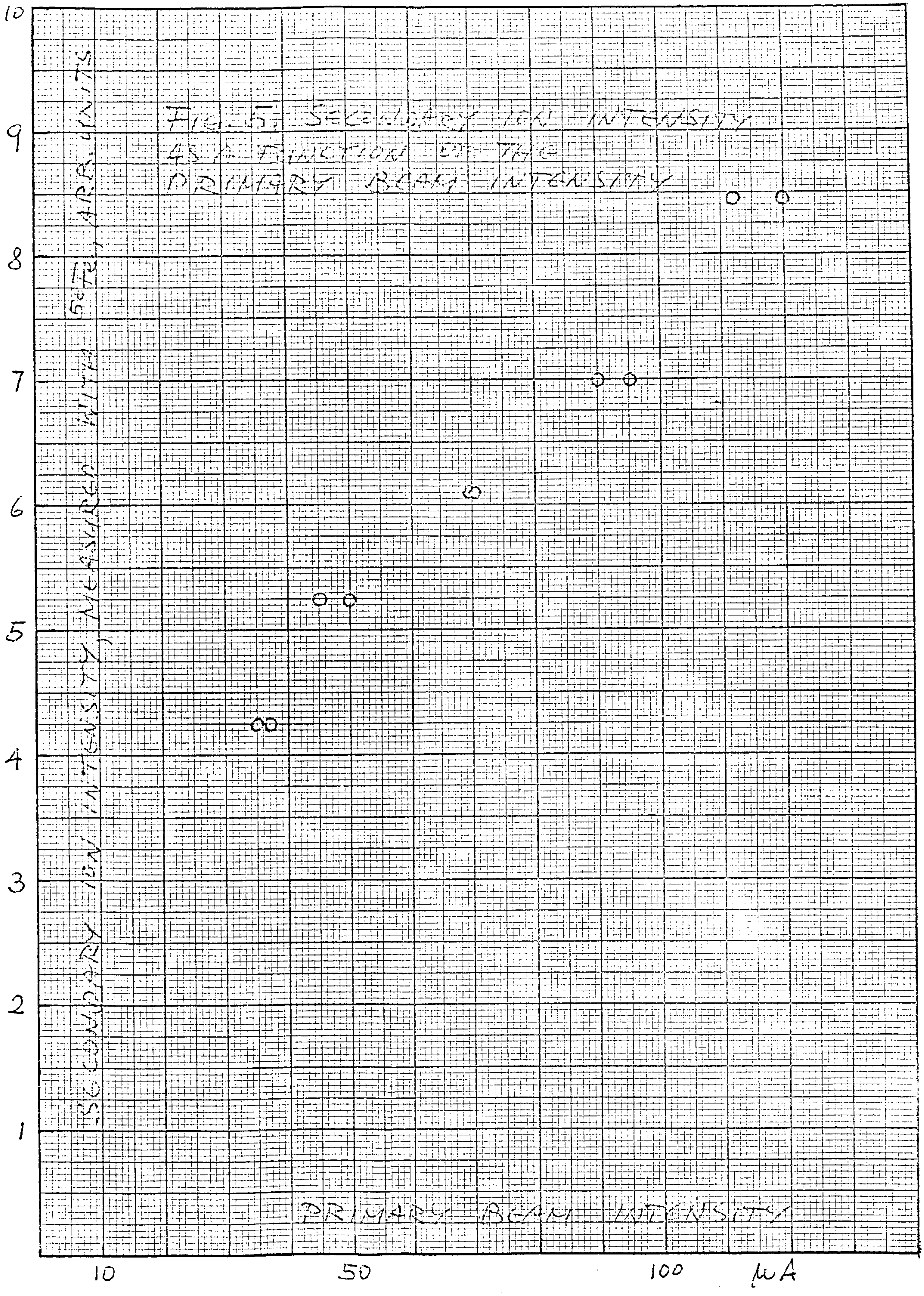


Figure 4. Copper



PRIMARY BEAM, OIL COOLER DISPLACEMENT

RECORDER TROUBLE

X 1000

12 14 16 18 20 23 26 28 32 36 40 56 65 181

X 1000

12 14 16 18 20 23 26 28 32 36 40 63

40

FIG. 6

PRIMARY BEAM; AIR cooled DEFLECTION

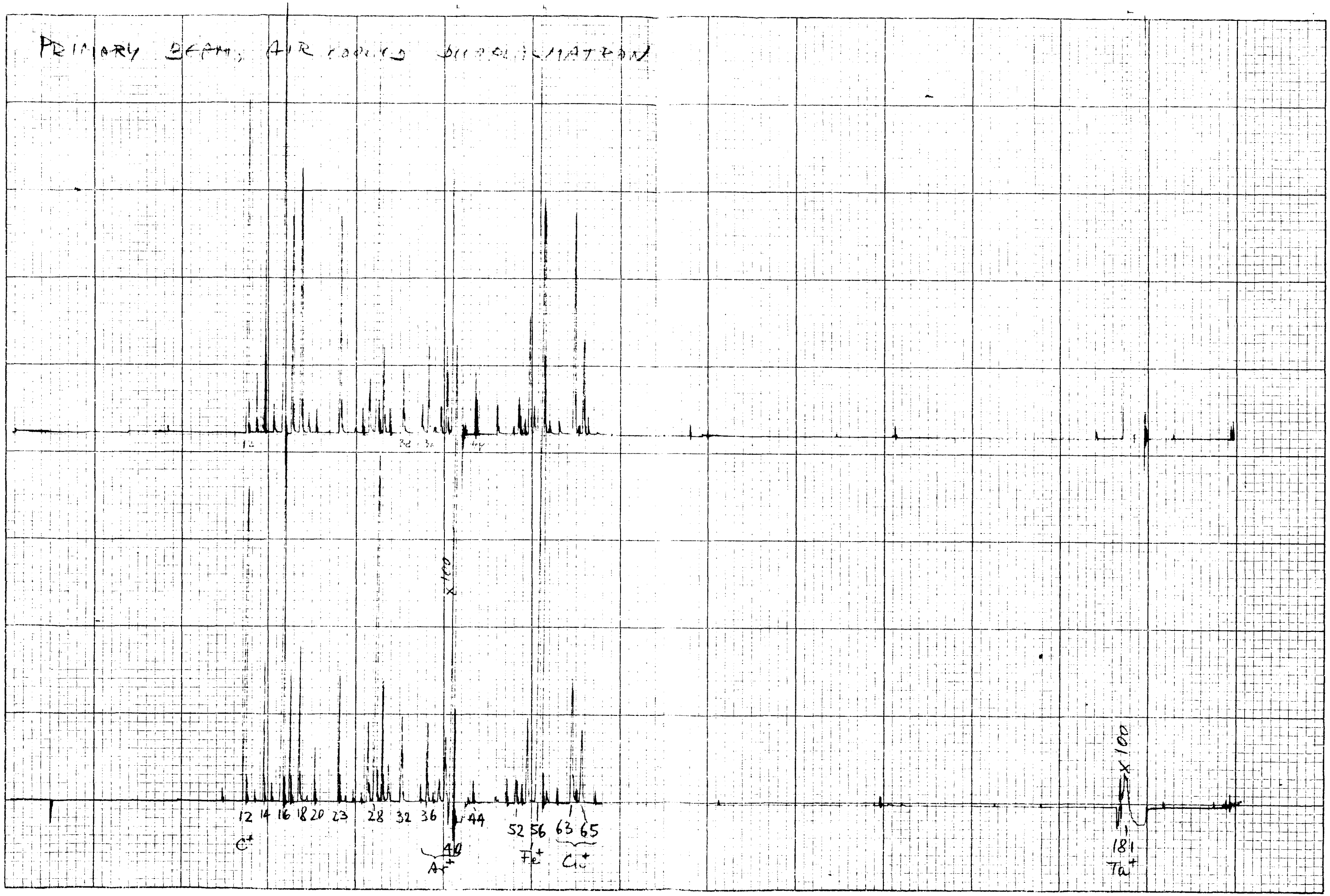


FIG. 7

PRIMARY 35mm, AIR COOLED

DUOPLASMATRON

TUNGSTEN FILAMENT

REMOVABLE ANODE TYPE

$10^{13}\Omega$ INPUT RESISTOR

100 mV range

10 X TO THE INCH 359 SL.
KEUFFEL & ESSER CO.

+1000

X1000

10 mV range

100 mV range

23 Na^+

36 40

Ar^+

56 Fe^+

12

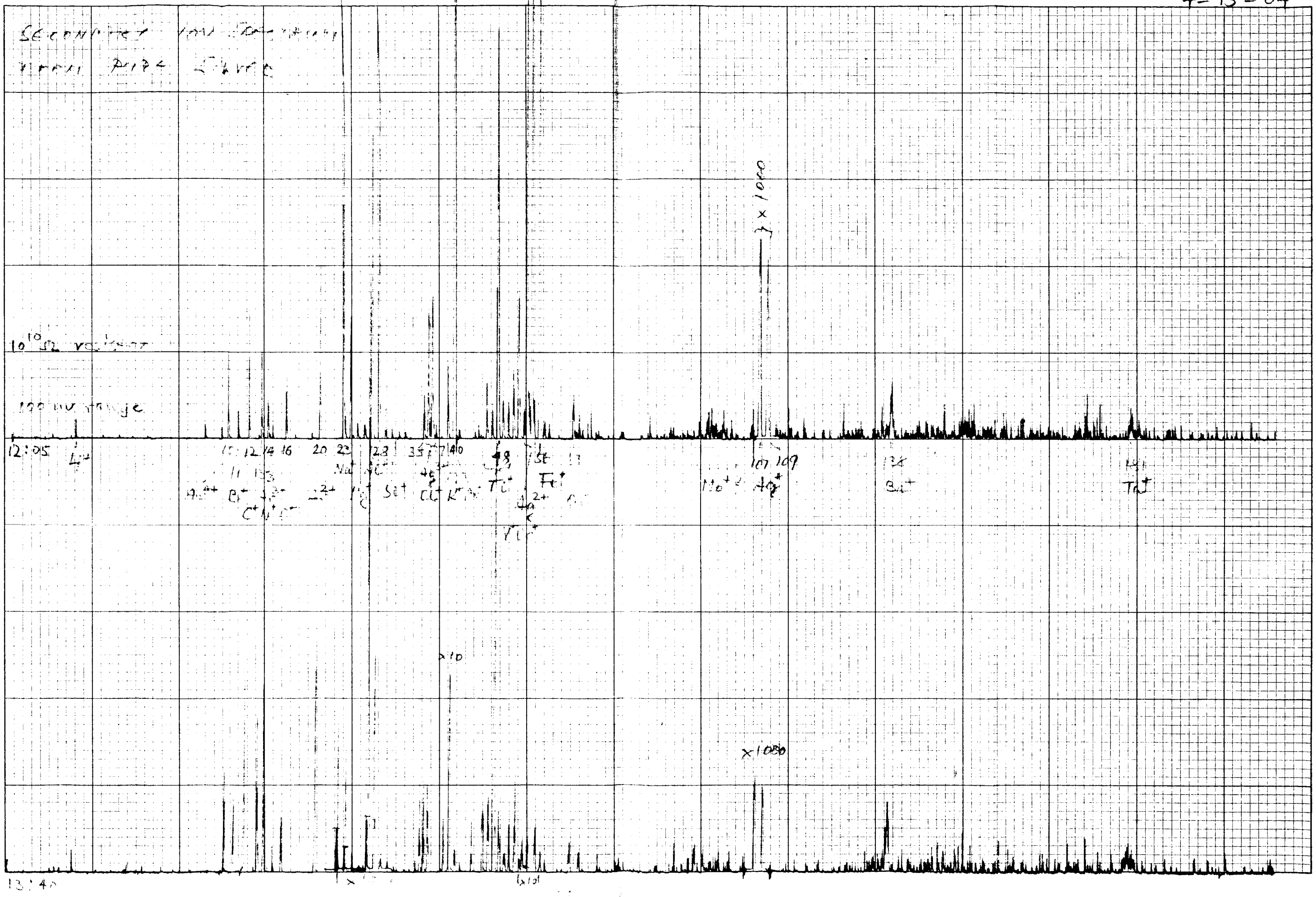
28

131

181 Ta

181 Ta^+

4-15-64



4-14-64

SECONDARY ION SPECTRUM
FROM PURE COPPER

$10^{10}\ \Omega$
100 mV

12 28 15:20

×1000

Cu^{3+}
Cu^{+} K^{+}

Li^{+} C^{3+} O^{+} F^{2+} Na^{+} Al^{2+} Si^{+} Cl^{2+} K^{+} Cr^{+} Fe^{+} Cu^{+} Cu_2^{+} Tl^{+}

12½ 16 20 23 24 28 35 40 52 56 126 181

T = .10

359-5L
10 X 10 TO THE INCH
KEUFFEL & ESSER CO.
MADE IN U.S.A.

4-15-64

SECONDARY ION SPECTRUM

HIGH PURE CHROMIUM

$10^{10}\Omega$

100 MV

X100

X100

359-5L
10 X 10 TO THE INCH
KEUFFEL & ESSER CO.

4-23-64

Secondary ion spectrum from NBS standard #165

14:50

recorder trouble

X 10

X 100

X 400

X 1000

X 1

X 1/10

15:10

12 16 20 24, 27 28 35 40 48 56 58 64 112

C^+ Al^+ O^+ Fe^{3+} Al^{2+} Ti^{2+} Fe^{2+} Fe_2^+

FIG. 12

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TELEPHONE: HOLBORN 6989

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Report

ON

MATTHEY SPECTROGRAPHICALLY STANDARDISED

SILVER RODS

LABORATORY No. 24757 CATALOGUE No. J.M.50

In any reference to this material both the above numbers should be quoted.

GENERAL

This material is supplied in the form of rod 7 mm. diameter and 10 cm. long and is of a high degree of purity.

SPECTROGRAPHIC EXAMINATION

A spectrographic examination was made by means of a constant current D.C. arc, taking 5.6 amps., between pure graphite electrodes. Weighed quantities of the sample were arced in thin-walled anode cups against a horizontal machined electrode as the cathode, both electrodes being water-cooled.

The spectra were photographed on an Ilford Long Range Spectrum plate with a flat-field Medium Spectrograph.

Estimates of the quantities of impurities present were made by visual comparison of the spectra with those of synthetic standards, arced in a manner similar to that used in the test.

Element	Estimate of Quantity Present parts per million
Bismuth, Cadmium, Copper, Iron, Magnesium, Sodium	each element less than 1

The following elements were specifically sought but not detected, i.e., either they are not present or they are below the limits of detection by the described examination procedure.

Al, As, Au, B, Ba, Be, Ca, Co, Cr, Cs, Ga, Ge, Hf, Hg, In, Ir, K, Li, Mn, Mo, Nb, Ni, Os, P, Pb, Pd, Pt, Rb, Re, Rh, Ru, Sb, Se, Si, Sn, Sr, Ta, Te, Ti, Tl, V, W, Zn, Zr.

During fabrication some surface contamination is unavoidable and for this reason all samples used during this spectrographic analysis have been pickled in concentrated nitric acid before examination.

October, 1961.

JOHNSON, MATTHEY & CO., LIMITED
Chemical Division

Report

ON

MATTHEY SPECTROGRAPHICALLY STANDARDISED

COPPER RODS

LABORATORY No. 34325 CATALOGUE No. J.M.30

In any reference to this material both the above numbers should be quoted.

GENERAL

These rods 5 mm. in diameter and 15 cm. long, were prepared from specially refined copper and are of a high degree of purity.

SPECTROGRAPHIC EXAMINATION

A spectrographic examination was made by means of a constant current D.C. arc, taking 5.6 amps., between pure graphite electrodes. Weighed quantities of the sample were arced in thin-walled anode cups against a horizontal machined electrode as the cathode, both electrodes being water-cooled.

The spectra were photographed on an Ilford Long Range Spectrum plate with a flat-field Medium Spectrograph.

Estimates of the quantities of impurities present were made by visual comparison of the spectra with those of synthetic standards, arced in a manner similar to that used in the test.

Element	Estimate of Quantity Present parts per million
Iron	2
Lead	2
Nickel	1
Silver	1
Cadmium, Magnesium, Manganese, Silicon	each element less than 1

CHEMICAL ANALYSIS: Selenium and tellurium were not detected in the copper by chemical analysis using a 150 gm. sample. The limit of detection of selenium and tellurium is 0.0002%.

OXYGEN: After heating for half an hour at 800°C in hydrogen a metallographic examination failed to show any signs of the presence of oxygen in the sample.

The following elements were specifically sought but not detected, i.e., either they are not present or they are below the limits of detection by the described examination procedure.

Al, As, Au, B, Ba, Be, Bi, Ca, Co, Cr, Cs, Ga, Ge, Hf, Hg, In, Ir, K, Li, Mo, Na, Nb, Os, P, Pd, Pt, Rb, Re, Rh, Ru, Sb, Se, Sn, Sr, Ta, Te, Ti, Tl, V, W, Zn, Zr.

During fabrication some surface contamination is unavoidable and for this reason all samples used during this spectrographic analysis have been pickled in nitric acid before examination.

April, 1963.

JOHNSON, MATTHEY & CO., LIMITED
Chemical Division

JOHNSON MATTHEY & CO., LIMITED

73/83, HATTON GARDEN, LONDON, E.C.1.

TELEPHONE: HOLBORN 989

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Report

ON

MATTHEY SPECTROGRAPHICALLY STANDARD

CADMIUM RODS

27057 170

LABORATORY No. CATALOGUE No.

GENERAL *In any reference to this material both the above numbers should be quoted.*

This material is supplied in the form of rods 8 mm. diameter and 10 cm. long.

SPECTROGRAPHIC EXAMINATION

A spectrographic examination was made by means of a constant current D.C. arc taking 5.6 amps., between pure graphite electrodes. Weighed quantities of the sample were arced in thin-walled anode cups against a horizontal machined electrode as the cathode, both electrodes being water-cooled.

The spectra were photographed on an Ilford Long Range Spectrum plate with a flat-field Medium Spectrograph.

Estimates of the quantities of impurities present were made by visual comparison of the spectra with those of synthetic standards arced in a manner similar to that used in the test.

Element	Estimate of Quantity Present parts per million
Lead	1
Copper, Magnesium, Silver	each element less than 1

The following elements were specifically sought but not detected i.e. either they are not present or they are below the limits of detection by the described examination procedure.

Al, As, Au. B, Ba, Be, Bi, Ca, Co, Cr, Cs, Fe, Ga, Ge, Hf, Hg, In, Ir, K, Li, Mn, Mo, Na, Nb, Ni, Os, P, Pd, Pt, Rb, Re, Rh, Ru, Sb, Sc, Si, Sn, Sr, Ta, Te, Ti, Tl, V, W, Zn, Zr.

During fabrication some surface contamination is unavoidable and for this reason all samples used during this spectrographic analysis have been pickled in dilute nitric acid before examination.

JOHNSON, MATTHEY & CO. LIMITED.
Chemical Division.

February 1962.